PATENT SPECIFICATION (11) 1 407 331

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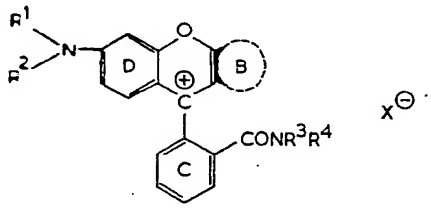
(19)

(54) COLOURATION PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the colouration of synthetic polymeric materials in particular polymeric materials comprising polymers and copolymers of acrylonitrile by the application thereto of a certain class of dyestuffs of the fluoran series.

Thus according to the present invention there is provided a process for the colouration of synthetic polymeric materials in particular polymers or copolymers of acrylonitrile which comprises applying thereto dyestuffs of the general Formula I



(I)

wherein R^1 and R^2 are independently hydrogen or optionally substituted alkyl preferably lower alkyl groups, B is an optionally substituted phenylene or naphthylene ring, R^3 and R^4 are independently, optionally substituted lower alkyl or aryl groups or R^3 and R^4 together can form a heterocyclic ring with the amide nitrogen atom, the rings C and D may optionally carry further substituents and X is an anion.

By the term lower alkyl group is meant an alkyl group of from one to four carbon atoms.

Examples of the Groups R^1 and R^2 include hydrogen, methyl, ethyl, propyl, isopropyl, n - butyl and tert.butyl.

The ring B may be a phenylene or naphthylene ring and may be optionally substituted, preferably by one or more of the following substituents, alkyl, aralkyl, aryl, acyl, alkoxy, aryloxy, halogen, cyano, nitro, a group of the formula —$COOR^5$, —$CONR^6R^7$, —$SO_2NR^6R^7$ or —NR^8R^9 wherein R^5 is lower alkyl, R^6 and R^7 are independently hydrogen or optionally substituted lower alkyl or aryl or together form a heterocyclic ring with the amide N atom and R^8 and R^9 are independently hydrogen, or optionally substituted lower alkyl, aralkyl, aryl or acyl or R^8 and R^9 taken together are a divalent radical optionally containing one or more hetero atoms forming a ring with the nitrogen atom.

Specific examples of such optional substituents in the ring B include chlorine, methyl, benzyl, phenyl, acetyl, benzoyl, methoxy, phenoxy, bromine, cyano, nitro, methoxycarbonyl, carbo - N,N - diethylamide, sulphon - N,N - dimethylamide, N,N-diethylamino, amino, acetylamino, ethylamino, benzylamino, anilino, N - methylanilino, p - toluidino, piperidino and morpholino.

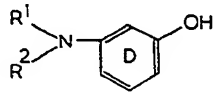
[Price 33p]

Examples of groups represented by R^3 and R^4 include ethyl, methyl, propyl, n-butyl, iso - butyl and when R^3 and R^4 are taken together with the amide nitrogen atom to form a ring include the piperidyl and morpholinyl rings.

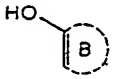
Optional additional substituents which may be present in the rings C and D include chlorine, bromine, methyl, methoxy and nitro.

Examples of the anion X include chloride, bromide, iodide, tetrachlorozincate, bisulphate, nitrate, sulphate, sulphamate, phosphate or borate or organic anions such as acetate, propionate, methosulphate, p - tolylsulphonate, and naphthalene - 2,5-disulphonate. In those cases where the anion is polyvalent the dyestuffs will contain a corresponding molar proportion of the cationic part of the dyestuff.

The dyestuffs used in the present invention may be obtained by known methods for example by condensation of phthalate anhydride or a substituted derivative thereof with the appropriate optionally substituted meta-aminophenol of the general formula



wherein R^1, R^2 and D are as hereinbefore defined, followed by condensation of the product with a compound of the formula



wherein B is hereinbefore defined, followed by conversion of the carboxylic acid group to a group CO—NR^3R^4 and solubilisation by salt formation. Dyestuffs of this type have been described in the art.

Colouration of the polymeric material may be carried out by applying the dyestuff from aqueous solution.

The polymeric materials may be for example in the form of tapes, fibres, films, threads or textile materials generally.

The colouration process of the present invention may be applied to polymeric materials generally including polyamides and polyesters, in particular acid modified polyamides and polyesters but is considered especially valuable for application to the dyeing or printing of polyacrylonitrile and copolymers containing acrylonitrile residues. Blends of different polymeric materials either synthetic or natural may also be used.

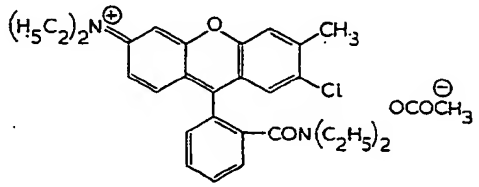
The colouration process may be carried out by applying the dyestuff from acid, neutral or slightly alkaline aqueous dyebath, i.e. at a pH of from 3 to 8, at temperatures between 40° C and 120° C preferably between 80° C and 120° C or by printing techniques. Printing techniques which may be used include the known methods in which the usual thickners and optional printing aids are added and final fixation of the dyestuff takes place in the usual manner, for example by steaming.

The dyeings give bright shades of excellent fastness to light, washing and heat treatment.

The invention is illustrated by the following examples in which all parts and percentages are by weight except where otherwise stated.

Example 1.

100 parts of polyacrylonitrile fibre are immersed in 3,000 parts of water containing 1 part of a dyestuff of the formula:—

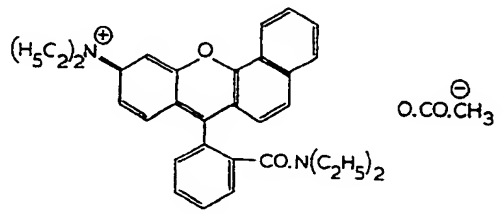


1 part of sodium acetate and 0.6 parts of acetic acid at 60° C. The temperature is raised slowly to 100° C, and dyeing continued at this temperature for 90 minutes.

The resulting dyeing has an attractive scarlet shade and excellent fastness to light, washing and heat treatment.

Example 2.

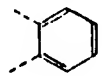
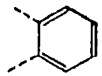
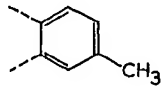
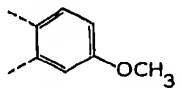
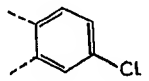
100 Parts of polyacrylonitrile fibre are dyed with 1 part of a dyestuff of formula:—

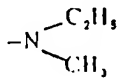
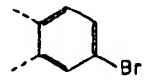
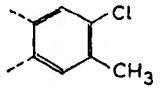
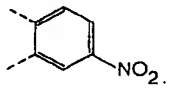


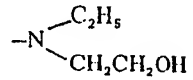
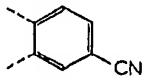
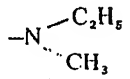
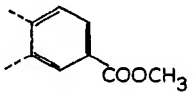
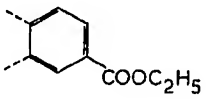
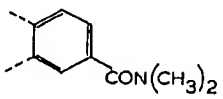
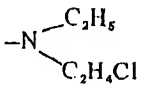
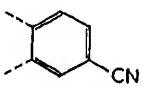
using the method of Example 1. A bright bluish-red dyeing with excellent fastness to light, washing and heat-treatment is obtained.

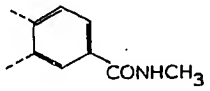
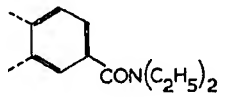
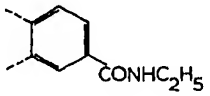
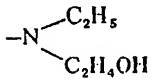
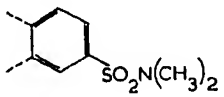
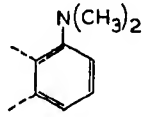
Examples 3—31.

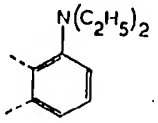
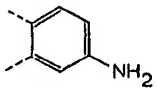
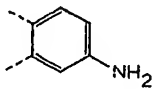
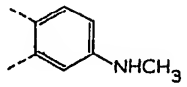
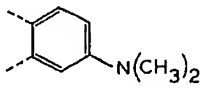
Further dyes of structure (I) which can be applied by the method of Example 1 are shown in the following table together with the shade on polyacrylonitrile fibres.

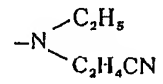
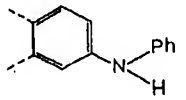
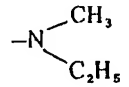
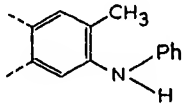
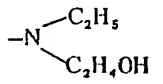
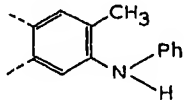
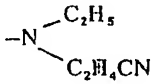
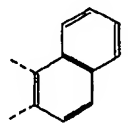
Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on poly-acrylonitrile
3	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$		Cl^-	Orange
4	$-N(C_2H_5)(CH_2CH_2CN)$	$-N(CH_3)_2$		$\frac{1}{2}SO_4^{2-}$	Orange
5	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$		Cl^-	Orange
6	$-N(C_2H_5)_2$	$-N(CH_3)_2$		$\frac{1}{2}ZnCl_4^{2-}$	Scarlet
7	$-N(CH_3)_2$	$-N(C_2H_5)_2$		Cl^-	Scarlet

Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on polyacrylonitrile
8		$-N(CH_3)_2$		$\frac{1}{2}SO_4^{2-}$	Scarlet
9	$-N(CH_3)_2$	$-N(C_2H_5)_2$		Cl^-	Scarlet
10	$-N(C_2H_5)_2$	$-N(CH_3)_2$		CL^-	Reddish-yellow
11	$-NHCH_3$	$-N(C_2H_5)_2$		Cl^-	Orange
12	$-NHC_2H_5$	$-N(CH_3)_2$		Cl^-	Orange

Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on polyacrylonitrile
13		$-N(C_2H_5)_2$		$\frac{1}{2}SO_4^{2-}$	Reddish-yellow
14		$-N(CH_3)_2$		Cl^-	Reddish-yellow
15	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$		$\frac{1}{2}ZnCl_4^{2-}$	Reddish-yellow
16	$-N(CH_3)_2$	$-N(C_2H_5)_2$		Cl^-	Reddish-yellow
17		$-N(C_2H_5)_2$		Cl^-	Reddish-yellow

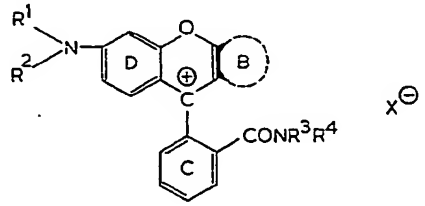
Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on polyacrylonitrile
18	$-N(C_2H_5)_2$	$-N(CH_3)_2$		$\frac{1}{2}SO_4^{2-}$	Reddish-yellow
19	$-N(CH_3)_2$	$-N(CH_3)_2$		Cl^-	Reddish-yellow
20	$-N(C_2H_5)_2$	$-N(CH_3)_2$		$\frac{1}{2}SO_4^{2-}$	Reddish-yellow
21		$-N(CH_3)_2$		Cl^-	Reddish-yellow
22	$-N(C_2H_5)_2$	$-N(CH_3)_2$		Cl^-	Red

Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on polyacrylonitrile
23	$-N(CH_3)_2$	$-N(C_2H_5)_2$		$\frac{1}{2}SO_4^{2-}$	Red
24	$-N(C_2H_5)_2$	$-N(CH_3)_2$		Cl^-	Dull green
25	$-N(CH_3)_2$	$-N(C_2H_5)_2$		$\frac{1}{2}SO_4^{2-}$	Dull green
26	$-N(C_2H_5)_2$	$-N(CH_3)_2$		Cl^-	Dull green
27	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$		$\frac{1}{2}SO_4^{2-}$	Dull green

Example	$-NR^1R^2$	$-NR^3R^4$	Ring B	X^-	Shade on polyacrylonitrile
28		$-N(CH_3)_2$		Cl^-	Dull green
29		$-N(C_2H_5)_2$		Cl^-	Black
30		$-N(CH_3)_2$		$\frac{1}{2}ZnCl_4^{2-}$	Black
31		$-N(C_2H_5)_2$		Cl^-	Bluish-red

WHAT WE CLAIM IS:—

1. A process for the colouration of synthetic polymeric materials which comprises applying thereto dyestuffs of the general Formula I



(I)

wherein R^1 and R^2 are independently hydrogen or optionally substituted alkyl groups, B is an optionally substituted phenylene or naphthylene ring, R^3 and R^4 are independently, optionally substituted lower alkyl or aryl groups or R^3 and R^4 together can form a heterocyclic ring with the amide nitrogen atom, the rings C and D may optionally carry further substituents and X is an anion.

2. A process as claimed in Claim 1 wherein R^1 and R^2 are lower alkyl groups.

3. A process as claimed in Claim 1 or Claim 2 wherein the dyestuff is applied to polymeric material from aqueous solution.

4. A process as claimed in any one of the preceding claims wherein the polymeric material is polyacrylonitrile or a copolymer containing acryonitrile residues.

5. A process as claimed in any one of the preceding claims wherein the dyestuff is applied from an acid, neutral or slightly alkaline aqueous dyebath at a pH of from 3 to 8 at a temperature of between 40° and 120° C.

6. A process as claimed in Claim 5 wherein the temperature is between 80° and 120° C.

7. A process as claimed in any one of the preceding claims wherein the dyestuff is applied by a printing technique.

8. A process according to Claim 1 with reference to any one of Examples 1 to 31.

9. Polymeric materials whenever coloured by a process as hereinbefore described and claimed.

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